A SECOND SET OF EXPERIMENTS USING HYDROLYZABLE POLYMERS TO PRESERVE WATERLOGGED WOOD

C. Wayne Smith

ABSTRACT

In this study, methyltrimethoxysilane (MTMS), a hydrolyzable, multi-functional alkoxysilane polymer and Q9-1315, a MTMS alkoxysilane polymer diluted with methanol, were used in conjunction with acetone dehydration to conserve waterlogged wood. Three groups of wood were used as samples for study. The Group 1 samples, waterlogged tongue depressors, were treated using acetone dehydration followed by immersion in MTMS. After using the acetone/MTMS displacement method, images of the treated wood were obtained using an environmental scanning electron microscopic, and were compared to similar images of non-waterlogged samples of the same wood samples, providing data on the ability of the polymer to preserve the micro-structure of the wood. A waterlogged plank from a submerged 17th-century architectural feature, from Port Royal, Jamaica, was divided into four sections to form the Group 2 samples. Two sections of this plank were treated by using MTMS on one section and Q9-1315 on another. The remaining two sections of wood were used to calculate the water content of the wood. The Group 3 samples consisted of 18 waterlogged treenails extracted from the frames of La Salle's vessel, *La Belle*, which sank off the coast of Texas in 1686. Eight of the Group 3 treenails were treated using MTMS immersion after dehydration in acetone. Eight other Group 3 treenails were treated using acetone dehydration followed by immersion in Q9-1315. The remaining two were used as controls for comparison. The nuclear magnetic resonance spectra of the samples from these Groups indicate that when waterlogged timbers are immersed in MTMS, resins are formed through self-condensation. The hypothesis of these experiments is that alkoxysilane polymers are sufficient to preserve the diagnostic attributes of wooden artifacts.

BACKGROUND AND INTRODUCTION

In his introduction to the *Proceedings of the ICOM Waterlogged Wood Working Group Conference, Ottawa, 1981*, Colin Pearson outlined the history, structure and evolution of the ICOM Committee for Conservation Working Groups. As noted in his historical perspective of the Waterlogged Wood Working Group, he observed that at the meeting of the Working Group in Zagreb (1978) an initial list of eight areas of research were outlined (Pearson, 1981). These included the use of detergents, tetraethyl ortho silicate, freeze-drying, analysis of polyethylene glycol (PEG), organic polymers, irradiation techniques and other problems connected with the salvage of waterlogged wood. Many of these treatment strategies have proven to be less than totally reversible. However, the Zagreb list is an excellent indicator that the science of waterlogged wood conservation has advanced, and that wood conservators have been industrious in their pursuit of better treatment strategies.

In just a few years, several areas of waterlogged wood research have blossomed, due to the hard work of dedicated conservators. Cliff McCawley, David Grattan and Clifford Cook have advanced research into the effects of PEG/freeze-drying waterlogged wood (McCawley, 1981, Grattan, 1984). At the same time, Per Hoffman conducted some invaluable studies observing that wood structures do not degrade at uniform rates, which led to his development of a highly effective, two-phase PEG-treatment strategy (Hoffmann, 1984). ARC-Nucleart has advanced studies in the preservation of waterlogged wood by impregnation with resins, which are then hardened using radiation (Ginier-Gillet, 1984). Additionally, they have worked successfully in treating larger artifacts using PEG impregnation followed by freeze-drying.

Although contributions to the discipline of waterlogged wood conservation continue, some of the long-term problems of treatments using PEG are being realized. In his address at the Ottawa ICOM Conference, Dr. Allen Bronstein, a senior chemist at Union Carbide Company, addressed the complexities of wood conservation and many factors related to the degradation of PEG (Bronstein, 1981). During the discussion, Cliff McCawley touched on the topic of the effects of metal salts on the degradation of PEG. In retrospect, this has become a topic of great concern. In recent years, the problem of PEG decomposition and the formation of chemical complexes, including aldehydes and ferrous, ferric and cupric salts, has become a pressing issue. Indeed, some of our finest examples of conserved waterlogged wood are on the verge of disintegration due to our inability to control oxidation, miscibility and chemical reactivity of PEG with oxides and compounds found naturally in waterlogged timbers.

This experiment investigates the use of trifunctional polyols to both stabilize and maintain the physical attributes of waterlogged wood samples, as suggested by Bronstein. (Bronstein, 1981) However, instead of directing research at creating “very hard and durable finishes,” as he suggests, this experiment focuses on impregnating a variety of waterlogged wood samples with a self-condensing polymer, in such a way as to cause formation of resins throughout the pore structure of the wood. There are benefits to this type of resin-forming chemical reaction. Displacement of water with the self-condensing polymer methyltrimethoxysilane (MTMS) does not appear to distress waterlogged wood. The low viscosity of MTMS allows for the thorough impregnation of waterlogged wood using either ambient or low vacuum processes. Using trace amounts of water, the alkoxysilane condenses, forming complex polymers that do not cause cell wall distortion or appreciable shrinkage. Post-treatment microscopic and NMR evaluation of the treated wood indicates that complex resins are formed throughout the wood. These resins are bound to the cell wall structures, giving the wood both strength and durability. Additionally, the wood is aesthetically pleasing without the waxy, dark coloration associated with PEG-treated wood.

Notably, the wood treatment strategies outlined in this experiment are not reversible. Considering the chemical structure of wood, however, few conservation materials used as bulking agents are truly reversible. This, in part, is due to the polymer nature of wood. Lignin, for instance, is a natural polymer composed of coniferyl alcohol and other compounds. Cellulose is a linear polymer with notably high concentrations of hydroxyl groups which form microfibrils. Even the starches found in wood consist of glucose polymers which contain amylose and amylopectin (Mills, 1994). This, in part, explains the non-reversible nature of PEG. PEG itself is a polymer composed of poly(ethylene oxides) polymerized from ethylene oxide. When introduced into wood as a bulking agent, PEG chemically bonds to cell walls, making complete reversal impossible. The polymer nature of wood also explains why alkoxysilane polymers are effective bulking and stabilizing agents. When introduced into an organic substrate, silanes form Si-OH groups that condense to form cross-links that are more stable than bonded PEG in a similar substrate. As prescribed by the ICOM activities committee in 1978, experimentation using alkoxysilane polymers and other organic polymers was, and still is, an essential phase of development in the discipline of organic artifact conservation.

CONSERVATION

Three groups of waterlogged wood samples were used for this experiment. The Group 1 wood

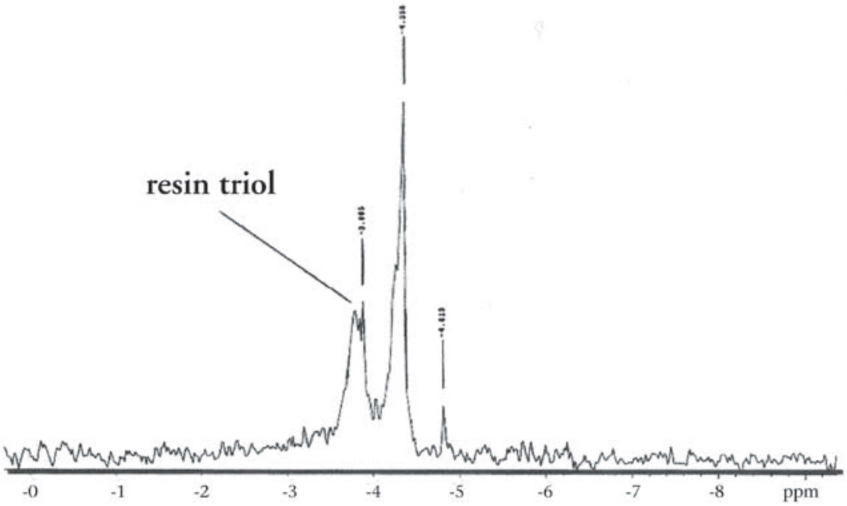

FIG. 1 **1H spectrum of the solid polymer formed from the MTMS. It is the formation of these polymers that preserves the structure and shape of the artifact.**

samples consisted of waterlogged wooden tongue depressors that had been immersed in tap water in sealed glass jars for eight years. The Group 2 waterlogged wood samples were sectioned from a large piece of archaeological wood from the marine excavations of the 1692 provenance of Port Royal, Jamaica. The Group 3 wood samples consisted of 18 treenails (hand-carved wooden dowels) that had been extracted from the frames and large timbers of the 17th-century shipwreck, *La Belle*, found off the coast of Texas. Each of these hand-carved lengths of wood were similar in circumference (26.66 mm average) and, for the most part, similar in length (128.70 mm average). Many of their surfaces bore diagnostic tool marks.

Nuclear magnetic resonance (NMR) spectra of waterlogged wood treated with alkoxysilane polymers indicate that in an aqueous environment, MTMS hydrolyzes to form a polymer triol as noted by C.V. Horie (Horie, 1999). This triol self-condenses to form a range of polymers in the 29Si spectra. The primary polymer has a methyl group and three siloxy bonds (*i.e.*, Si - O - Si). The second resultant silicon has only two bonds. The third is formed to the methyl group while the fourth bond is to the hydroxy group as in the 1H spectrum (fig. 1). One of the goals of these experiments was therefore to determine whether these polymers were sufficient to maintain the physical attributes, cell structure and aesthetics of the Group 1, Group 2, and Group 3 wood samples.

NMR analysis was also conducted to determine whether the waterlogged tongue depressors were sufficiently degraded to provide a valid substitute for archaeological wood in such an experiment. The spectra of the Group 1, as well as the archaeological wood samples of Group 2 and 3, were nearly identical to spectra reported by Michael Wilson, *et al*, in *The Degradation of Wood in Old Indian Ocean Shipwreck* (Wilson, 1993). To determine the physical integrity of the Group 1 wood samples, waterlogged control samples were oven-dried over a 24-hour period. In all cases, the degree of warping and shrinkage indicated that the waterlogged tongue depressors respond similarly to the air- or oven-dried waterlogged archaeological wood. Classroom conservation experiments have shown that waterlogged tongue depressors are good indicators of the effectiveness of traditional waterlogged wood treatment methods such as PEG, acetone/rosin and sucrose. This same type of waterlogged wood appears to work equally well as an indicator of the effectiveness of polymer preservation treatment strategies.

MATERIALS

Group 1 Waterlogged Tongue Depressors

Tongue depressors were chosen for use in this experiment because they are both easily obtained and relatively uniform in dimension, grain and color. To create a supply of waterlogged wood, thousands of white birch (*Betula papyrifera*) tongue depressors were placed into one-gallon glass jars filled with tap water. The jars were then sealed and stored in a cabinet. For this experiment, hundreds of tongue depressors, which had been immersed in tap water since June 2, 1992, were emptied into a plastic vat and rinsed with running tap water for two hours. Ten tongue depressors were randomly

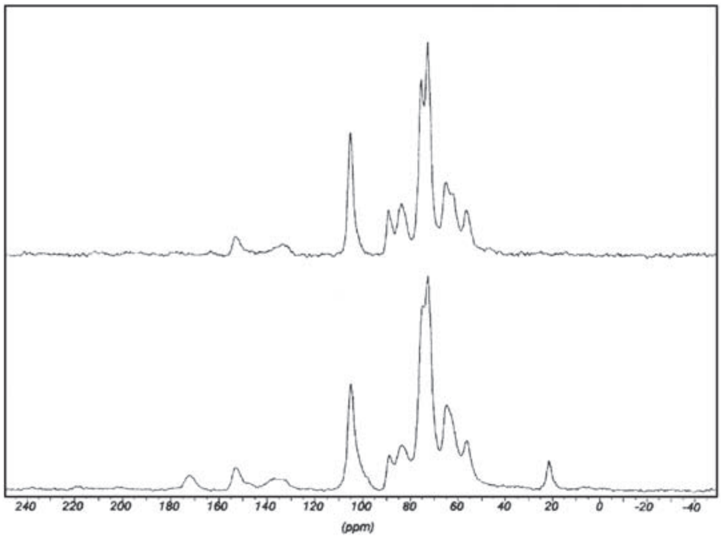

Fig. 2 **13C CP/MAS spectra of an untreated, non-waterlogged control tongue depressor (bottom) and an untreated, waterlogged tongue depressor (top).**

selected from the rinse vat and designated as air-dry samples, to determine the average water content of the wood of Group 1. Eighteen additional tongue depressors were randomly selected as Group 1 to undergo treatment using acetone dehydration followed by acetone/MTMS displacement.

The 13C CP/MAS spectrum for a Group 1 air-dried sample is illustrated at the top of figure 2. Long-term saturation in tap water has altered the chemical structure of the wood, apparent in the loss of the acetate resonances at 22 and 174 ppm, in comparison to the spectrum of a control tongue depressor that had not been waterlogged (fig. 2). The changes in these 13C spectra for birch tongue depressors are quite similar to those reported by Wilson, *et al*, (Wilson, 1993) for oak from shipwrecks. The 13C spectral signature and macroscopic observation of extensive warping and shrinkage following air-drying suggest that these samples provide a suitable model for the analysis of waterlogged wood.

Group 2 Waterlogged Archaeological Wood

A small plank of wood recovered during archaeological excavations at the submerged site of 17th-century Port Royal, Jamaica, was selected for the Group 2 wood samples. Based on cross-section microscopic analysis, the wood has been tentatively identified as *Pinus carabaea*, commonly known as slash pine or British Honduras pitch pine. Typically, this wood has a straight fine grain which is very uniform in texture. Since excavation from the 1692 provenance at Port Royal, the plank, which measures 12.32 cm wide, 14.73 cm long and 1.87 cm thick, had been desalinated and stored in fresh tap water. For this experiment, the plank was divided into four sections. Because it was waterlogged the wood was very fragile, so sectioning was accomplished using a long scalpel blade. Figure 3 illustrates the dimensions of the Group 2 samples.

Group 3 Waterlogged Treenails

The Group 3 artifacts were treenails, which were extracted from the timbers of the 17th century shipwreck, *La Belle*. Each piece of wood was roughly carved and slightly tapered in shape. After desalinization in freshwater baths for 24 months, the 18 treenails were surface-dried with paper towels and then weighed, measured and photographed (fig. 4).

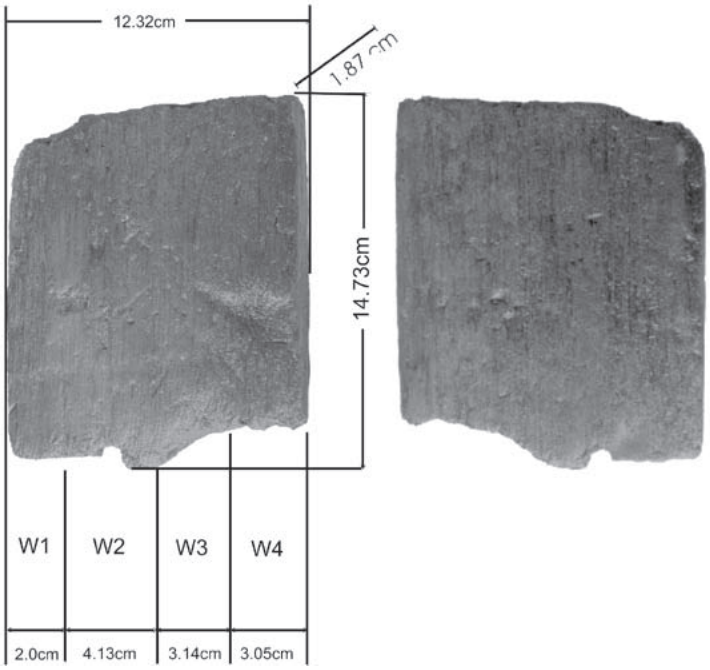

Fig. 3 **Surface characteristics, sections and dimensions of the waterlogged plank used for the Group 2 waterlogged wood samples. Top surface of the plank (left); obverse surface (right).**

FIG. 4 **Example of a waterlogged treenail.**

METHYLTRIMETHOXYSILANE AND Q9-1315

Methyltrimethoxysilane (MTMS) is a chemical monomer that reacts with water to form silane triol and methanol. The silane in turn condenses with available hydroxyl groups or other silanol monomers to form siloxane resins. The chemical formula for MTMS is $(CH_3O)_3\ SiCH_3$. Typically, MTMS is a solution of 97% methyltrimethoxysilane with 2% methyl alcohol, and 1% dimethyldimethoxysilane added. The condensation product of MTMS is a resin with a molecular weight of 226.

Q9-1315 is a complex solution, and consists of 44% methyltrimethoxysilane (by weight), mixed with 50% methyl alcohol, 4% isopropyl alcohol, 1% ethyl alcohol, and 1% dimethyldimethoxysilane. Like MTMS, Q9-1315 is generally a clear liquid, however because of the lower percentage of methyltrimethoxysilane and a higher percentage of alcohol, evaporation during treatment is greater, and there are fewer hydroxyl groups and other silanol monomers available to form resins.

Industrial-grade ethanol (certified to be 97.62% free of water) and acetone (certified to be 99.78% free of water) were used for all dehydration processes.

WATER CONTENT OF GROUP 1, 2 AND 3 WOOD SAMPLES

Percentage water content was calculated for each group of samples using the formula illustrated in figure 5.

$$\%H_2O = \frac{\text{Weight of the wet wood} - \text{Weight of the oven-dried wood}}{\text{Weight of the oven-dried wood}} \times 100$$

FIG. 5 **Formula used to calculate water content of tongue depressors and archaeological wood samples [10].**

Group 1 Wood

Ten randomly selected waterlogged tongue depressors were placed in a ventilated warming oven for 24 hours, set at 400°C. The average water content of the Group 1 oven dried samples was determined to be 215.96%.

Group 2 Wood

Following 24 hours in a vented warming oven, set at 400°C, wood section W1 went from a weight of 39.10 g to 4.4 g, representing a total weight loss of 88.49%. The water content was calculated to be 788.64%. Because of the uniform thickness and condition of the wood, the water content calculation for W1 was assumed to reflect the general state of degradation of the other sections of wood.

Prior to air-drying, W4, the second air-dried archaeological wood sample, had a mass of 104.3 g. W4 was placed in a fume hood and allowed to air-dry for 36 hours at ambient pressure and a constant room temperature of 760°F (24.40°C). Following drying, the sample weighed 10.3 g, representing a weight loss of 90.13%, representing 912.62% water content.

Group 3 Wood

The two waterlogged treenails, weighing 82.1 g and 68.2 g wet, were allowed to air-dry in a ventilated warming oven for 48 hours. After air-drying, the treenails weighed 34.48 g and 34.65 g, representing an average weight loss of 58.01% (138.11% water) and 49.19% (138.62% water) respectively.

TREATMENT METHODS

Group 1 Wood

After randomly selecting 18 Group 1 waterlogged tongue depressors from the rinse vat, each was surface-dried with paper towels and labeled incrementally with a felt-tip pen. Length, width, thickness and weight measurements were recorded for each sample.

Next, the wood samples were placed in a large beaker containing one liter of fresh, industrial-grade acetone. After 24 hours, they were transferred to a second beaker containing one liter of fresh acetone and dehydrated for an additional 24 hours. After 48 hours of dehydration, the Group 1 samples were transferred into a beaker containing one liter of methyltrimethoxysilane (MTMS). Then, the beaker was placed into a desiccator vacuum chamber with a reduced pressure environment of 5333.33 Pa (40 torr) for 6 hours. After 6 hours of acetone/MTMS displacement, the wood was allowed to sit in the solution at ambient pressure and room temperature for an additional 18 hours. The samples were removed from the MTMS solution and placed onto paper towels in a fume hood and air-dried for 2 hours. All of the samples were then placed into a large Ziploc bag along with an aluminum weighing dish containing 15 g of tap water. The bag was sealed, creating a closed, humid environment. After 24 hours of exposure to water vapor, the Group 1 wood was removed from the bag and allowed to air-dry in a fume hood. The treated wood was then measured in order to assess the conservation process.

Group 2 Wood

Two sections of the plank, W2 and W3, were chosen for treatment with alkoxysilanes. W2 was placed into a beaker containing one liter of industrial-grade acetone, and was dehydrated at ambient pressure and room temperature for 24 hours. The wood was then placed into fresh acetone for an additional 24 hours of dehydration. After 48 hours of dehydration, W2 was transferred to a beaker containing one liter of MTMS and placed into a desiccator vacuum chamber, where a reduced pressure of 5333.33 Pa (40 torr) was applied for 10 hours. The wood was left in the solution at ambient pressure and room temperature for an additional 12 hours. Following acetone/MTMS displacement, W2 was removed from the solution and placed into a Ziploc bag. An aluminum weighing dish containing 20 g of tap water was placed inside the Ziploc bag, in close proximity to W2. The bag remained sealed for 18 hours. The wood was then removed from the bag and placed in a ventilated fume hood for an additional 24 hours. After air-drying, the wood was weighed and measured.

Like W2, W3 was placed in a beaker containing one liter of industrial-grade acetone and dehydrated at ambient pressure and room temperature for 24 hours, and then transferred into another fresh liter of industrial-grade acetone for an additional 24 hours. The wood was then transferred to a beaker containing one liter of Q9-1315 and placed into a desiccator vacuum chamber. A reduced pressure of 5333.33 Pa (40 torr) was applied for 10 hours. The wood was left in the solution at ambient pressure and room temperature for an additional 12 hours. After acetone/Q9-1315 displacement, W3 was removed from the solution and placed in a Ziploc bag with a rag, dampened with 20 g of tap water. The bag was sealed and the wood was allowed to sit for 18 hours. The wood was then removed from the bag and placed in a ventilated fume hood for an additional 24 hours. After air-drying, the wood was weighed and measured.

Only trace amounts of water are necessary to ensure silanol Si-OH groups that can bond with OH structures in the wood. Accordingly, W2 and W3 samples were air-dried in close proximity to a dish containing 20 g of water.

Group 3 Wood

The sixteen treenails were first dehydrated in a series of three ethanol baths, each lasting one week. Then, the dehydration was continued in a series of three acetone baths, changed at two week intervals. For the last 10 hours of dehydration, the samples were placed in a large vacuum chamber and treated at a reduced pressure of 5333.33 Pa (40 torr). During this phase of dehydration, the samples were monitored closely to ensure that they remained immersed in the acetone.

Eight of the treenails were randomly selected and carefully transferred to a large beaker containing one liter of MTMS. The remaining treenails were transferred into a beaker containing one liter of Q9-1315. Both beakers were then placed in a vacuum chamber and treated at a reduced pressure of 5333.33 Pa (40 torr) for 24 hours. The treenails were then stored at ambient pressure in their respective polymers for an additional seven days.

All of the treenails were then removed from the solutions, surface dried with paper towels, and placed in a fume hood where they were allowed to air-dry for 24 hours.

OBSERVATIONS

Group 1 Wood

The average wet weight of the Group 1 wood was 5.62 g. After (MTMS treatment), the average weight was reduced to 2.59 g, representing a weight reduction of 53.83%. The average width of the air-dried waterlogged tongue depressors was reduced from 17.89 mm to 13.67 mm, representing a 23.58% reduction. The average length of the same samples was reduced from 152.37 mm to 151.74 mm, representing an average reduction of 0.71%. The average thickness of these samples was reduced from 0.17 cm to 0.15 cm, or -11.77%.

FIG. 6 **Control tongue depressor (top); eight MTMS-treated, waterlogged tongue depressors (below).**

The dimensions and the aesthetic attributes of the Group 1 MTMS-treated wood samples were well-maintained after treatment. Changes in length were minimal following treatment, with a reduction of only 0.41%, on average, after MTMS-treatment. Change in width of the samples was noticeably high, with an average post-treatment reduction of 11.11%. One control tongue depressor and eight MTMS-treated wood samples are illustrated in figure 6.

After air-drying, the color of the waterlogged tongue depressors had changed from a natural light yellow brown color (10 YR/8/2 Munsell), ranging from a light gray-brown (2.5Y/7/2 Munsell) to a darker brownish-gray (10 YR/6/2 Munsell).

Micro-Structure of the Group 1 Wood Samples

Cross-section samples of control, untreated wood, air-dried wood and MTMS-treated tongue depressor samples were analyzed using an environmental scanning electron microscope (ESEM). For analytical consistency, photographs of each sample were recorded at 1000-X amplification. Cell shape retention, cell wall integrity and general appearance were used to assess the effectiveness of the treatments.

In Figure 7, the left image is a 1000-X amplification of the cross-sectional surface of an untreated birch (*Betula papyrifera)* control tongue depressor showing uniformly shaped, thick-walled tracheids. In contrast, the tracheids in the waterlogged wood sample (right) are irregular in shape with the deterioration of the middle lamella. Figure 8 shows two views of the micro-structure of a Group 1, MTMS-treated sample of wood. Cell walls collapse is negligible, and there is very little distortion and structural loss of the middle lamella. In figure 9, two cross-section views indicate that after air-drying, the cellular structure of the Group 1 waterlogged wood samples collapsed, causing extreme shrinkage and distortion of the wood.

Group 2 Wood

Prior to air-drying, W1 weighed 39.10 g and measured 2.00 cm wide, 1.87 cm thick and 12.20 cm long. After 24 hours of oven-drying, the wood

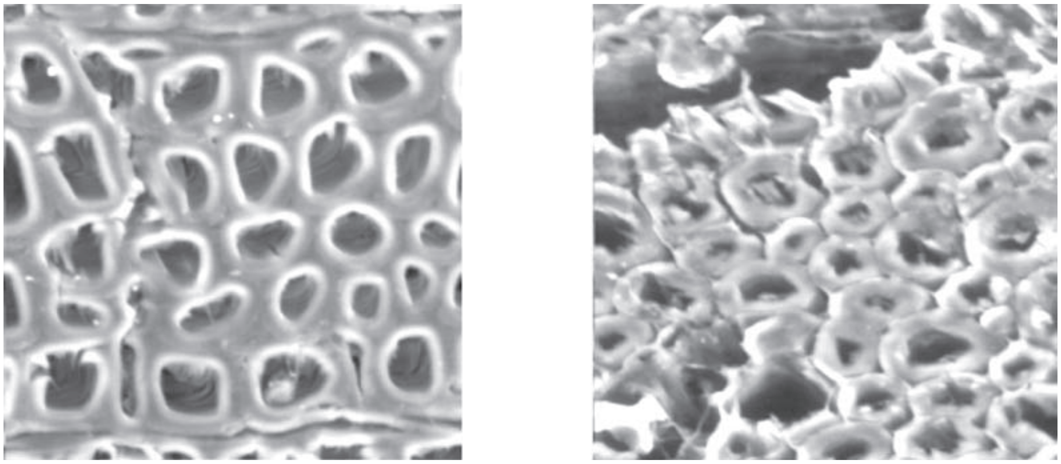

Fig. 7 **Control Group 1 tongue depressor on the left and image of a waterlogged Group 1 tongue depressor on the right, viewed at 1000X.**

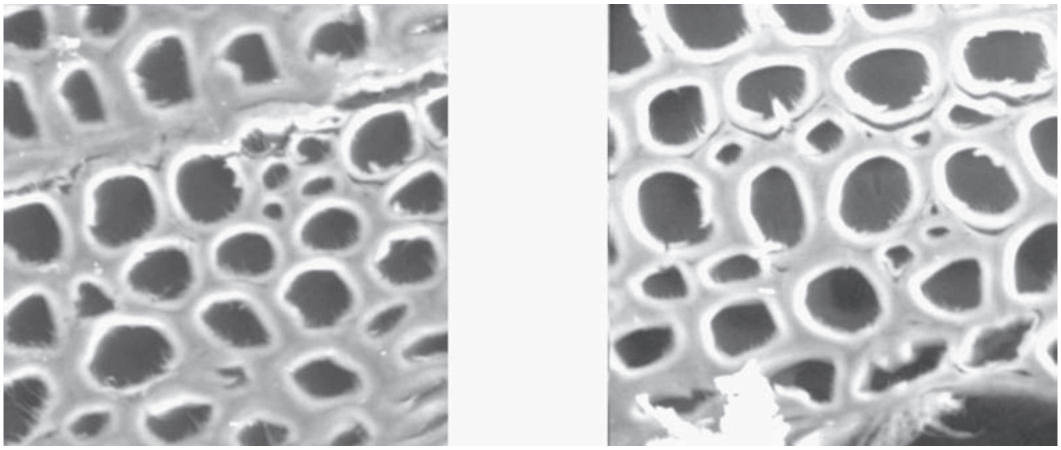

Fig. 8 **Two cross-section microscopic views (1000X) of a Group 1 tongue depressor treated using MTMS.**

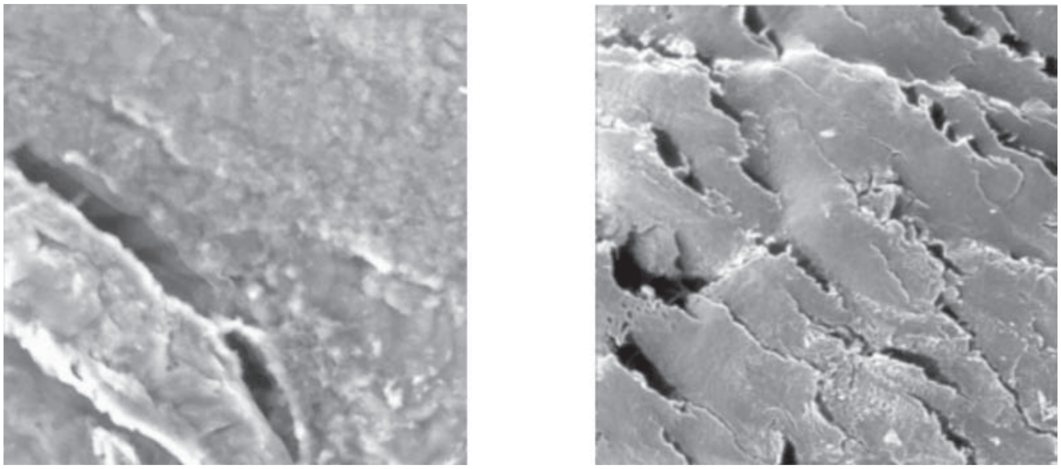

Fig. 9 **Two cross-section views of Group 1, air-dried wood samples. In both images, cellular distortion and collapse is apparent, resulting in extreme warpage and distortion.**

weighed 4.40 g, representing a loss of 34.70 g and an average change of -88.75%. The water content of this sample was calculated to be 788.64%. When removed from the warming oven, the wood had completely collapsed and fragmented into five sections. The final length and width of W1 was impossible to determine due to fragmentation during air-drying. Prior to treatment, the thickness of W1 was 1.87 cm thick. Average thickness of W1 wood fragments after treatment was 0.42 cm, representing a reduction in thickness of 77.54%.

W2 was sectioned from the plank adjacent to W1. This section of wood (W2) had a wet weight of 115.7 g and measured 4.13 cm wide, 1.86 cm thick and 14.68 cm long. W2 was designated for treatment in MTMS, after dehydration in acetone.

After treatment in MTMS, W2 appeared uniformly dry and light in color, and only slight dimensional changes were noted. The wet weight of sample W2 was reduced from 115.7 g to 28.7 g, representing a change of -75.20%. The width of W2 measured 4.13 cm prior to treatment, and after treatment it measured 3.96 cm, representing a change of -4.12%. The thickness of W2 prior to treatment was 1.86 cm, and after treatment, it measured 1.85 cm thick, indicating that no significant change had occurred in thickness. After treatment, W2 measured 14.63 cm, compared to its pre-treatment length of 14.68 cm, representing a change of -0.34%.

Prior to treatment, the entire plank of wood was dark brown in color (10 YR/3/3 Munsell), while after treatment, W2 was a light, gray-brown color (10 YR/6/2 Munsell). The surfaces of the wood showed no signs of checking and the wood looked very natural. After treatment, W2 was very light in weight, and since then has withstood extensive handling with no signs of deterioration or wear.

W3 was treated with Q9-1315, after an initial dehydration in acetone. The wet weight of W3 was 91.3 g, while after treatment, W3 weighed 26 g, representing a change of -71.52%. The width of the sample was reduced from 3.14 cm to 2.98 cm, representing a change in width of -5.10%. The thickness of W3 was reduced from 1.84 cm to 1.62 cm, representing a change of -11.96%. The wet length of W3 was 14.73 cm, and after treatment, it measured 14.54 cm, representing a change in length of -1.29%.

While shrinkage was more of a problem with sample W3, the end result was more aesthetically pleasing than W2. Prior to treatment, W3 was dark brown in color (10 YR/3/3 Munsell). After treatment, the wood was slightly darker (10 YR/4/2 Munsell) than W2. Both W2 and W3 wood samples were natural in appearance and dry to the touch. The post-treatment color of W2 and W3 are illustrated in figure 10.

FIG. 10 **Group 2 wood after treatment. W1, oven dried wood; W2, MTMS-treated wood; W3, Q9-1315-treated wood; W4, air-dried wood in vented fume hood. Note the comparatively lighter color of section W2.**

The remaining section of wood, W4, was treated by air-drying. W4 was the larger of the two air-dried samples from the original plank of waterlogged wood, and in comparison to W1, W4 was more similar in size to the sections of wood treated with alkoxysilane polymers. Prior to treatment, its wet weight was 104.3 g. After treatment, it weighed 10.3 g, representing a change of -90.13%. It width was reduced from 3.05 cm to 2.55 cm, representing a change in width of -16.39%. The thickness of the sample was reduced from 1.87 cm to 0.72 cm, a change of -61.50%. Post-treatment length of W4 was difficult to determine as the sample splintered into six large sections, each exhibiting gross distortion of its edges. Prior to air-drying, the sample measured 12.27 cm at it longest point. After treatment, W4 measured approximately 10.41 cm in length, representing a change of -15.16%. Figure 10 illustrates the post-treatment condition of samples W1, W2, W3 and W4.

The Group 2 samples were limited in number, simply because extraneous pieces of archaeological wood are in short supply for experimental purposes. The plank selected for experimentation was uniform in thickness and appeared to be uniformly soft to the touch. After drying, both samples W1 and W4 had deteriorated into a pile of splinters, making a comparison of pre-and post-treatment dimensions impossible. The wood was calculated to have the water content of 788.64%, based upon sample W1, which was considered to be more uniform than sample W4 (912.62% water content).

Group 3 Wood

Prior to treatment, the average percentage water content of the Group 3 waterlogged treenails was 321.55%, appreciably lower than the water content of 788.64% calculated for the Group 2 wood samples. During initial cleaning and desalination, the treenails were found to be less spongy than the sections of the plank (Group 2), and the wood was noticeably harder. Unfortunately, many of the ends of the treenails had either broken or been slightly splayed under the force of being removed from the ships timbers.

The Group 3 wood samples that were treated using MTMS alkoxysilane polymers experienced only slight changes in post-treatment weight and dimensions, in comparison to the Group 3 Q9-1315-treated wood. After treatment, the average weight of MTMS-treated treenails was 40.48 g, representing a percentage weight change of -45.74%. Treenails preserved using Q9-1315 polymer had an average weight of 39.32 g after treatment, representing a percentage weight change of -43.76%.

Group 3 treenails preserved using MTMS had an average change in length of -0.36 %. The change in length was higher for Q9-1315-treated treenails, with an average post-treatment length of 121.76 mm, representing a percentage shrinkage of 0.49%.

Similarly, the average change in diameter for the Group 3 MTMS-treated treenails was substantially less than the average change in diameter for Q9-1315-treated treenails. The post-treatment average diameter for MTMS-treated wood was 25.74 mm, a decrease of 3.42%. Q9-1315 treenails had an average decrease in post-treatment diameter of 9.36%.

The most noticeable difference between the MTMS and Q9-1315-treated treenails was color. In all cases, the color of the MTMS-treated wood is much lighter than the Q9-1315-treated wood, which tends to be darker in color with fewer wood grain and surface features visible.

DISCUSSION

NMR spectral analysis, ESEM analysis and empirical data indicate that the structural integrity of the Group 1 tongue depressors was sufficiently degraded so that the wood samples can be used to evaluate preservation treatments for waterlogged timbers from shipwrecks. Group 1 wood samples provide a reasonably homogeneous source of wood, which allows for the quantitative and qualitative analysis of the effectiveness of consolidants being tested for use in conserving waterlogged wood. The regularity of size and species and the availability of non-waterlogged control samples makes the Group 1 wood samples invaluable for waterlogged wood experimentation. Because of the inherent inconsistencies in waterlogged archaeological wood, similar comparative data would be very difficult to derive from archaeological samples.

MTMS-treated Group 1 wood samples were generally well-preserved. The average reduction in length was 0.41% after treatment, and the average reduction in width was 11.78%. The second figure seems high, but a comparison of the MTMS-treated samples to the untreated control tongue depressors shows that they are nearly the same, indicating that the treated wood was restored to the dimensions nearly identical to those of the control wood samples. The swelling that occurred in the tongue depressor during the waterlogging process had been greatly reduced after the wood was treated in MTMS. ESEM evaluation of these samples confirm that cell dimensions and shapes were similar to those of the control wood samples. A slight shrinkage of the middle lamella was noted after treatment.

Acetone/MTMS displacement of the Group 1 samples was conducted in a reduced pressure environment. In this environment, the boiling point of acetone is lowered, resulting in faster and more thorough evaporation of the solvent. Testing conducted in developing procedures for this experiment indicated that ambient pressure evaporation of acetone is sufficient to allow the uptake of MTMS without causing shrinkage or distortion of the wood being treated, while the use of a reduced pressure environment accelerated the displacement process.

After MTMS treatment, all of the Group 1 tongue depressors are slightly gray-brown in color (10YR 7/2 Munsell) when compared with the color of the control tongue depressors (10YR 8/4 Munsell). This shift in color is the result of changes in the wood caused by long-term immersion in water.

The Group 2 samples were highly degraded before treatment. The computed water content of the samples was between 788.64% and 912.62%, suggesting that degradation and resultant water content was reasonably uniform throughout the plank. Oven-dried sample W1 and air-dried W4 were much darker in color than sections W2 and W3. This is the result of extreme cellular collapse and warpage that occurred as the result of drying. Both samples of wood had disintegrated so much that accurate physical measurements could not be obtained.

The conservation of samples W2 and W3 was considered successful as their physical dimensions, surface textures, and individual characteristics were accurately maintained. Lower rates of shrinkage were observed in the MTMS-treated wood sample W2. This section of wood is also lighter in color than sample W3, which is darker due to the slightly higher degree of shrinkage that occurred as the result of treatment in Q9-1315. Indeed, this degree of shrinkage suggests that the Q9-1315 solution does not contain sufficient alkoxysilane polymers to preserve badly waterlogged wood.

Because MTMS is 97% pure with a 3% addition of alcohols, this polymer has better resin-forming capabilities than Q9-1315, which contains approximately 44% MTMS mixed with organic solvents and trace amounts of dimethyldimethoxysilane. Accordingly, the resin-forming capabilities of the Q9-1315 solution are insufficient to preserve the dimensional characteristics of the wood, which is evident from the slightly higher rates of shrinkage for sample W3.

The diagnostic attributes of W2 and W3 were preserved because, as a result of condensation, sufficient resins were formed to prevent cellular collapse of the wood. Waterlogged tongue depressors and the archaeological wood samples preserved with the MTMS solution, which has a higher percentage of hydrolyzable, multi-functional alkoxysilane polymers, were the best preserved specimens of the groups. In contrast, the Q9-1315 solution, which contained a lower percentage solution of the same multi-functional alkoxysilane polymers, was insufficient to preserve the diagnostic attributes of the wood.

After treatment, the diagnostic attributes of Group 3 waterlogged treenails treated with MTMS were visibly better than the Group 3 samples treated with Q9-1315. MTMS-treated treenails did not exhibit scalloped surface features associated with cellular collapse. The shrinkage in these artifacts was minimal (0.36% average length shrinkage). The average post-treatment diameter change for MTMS-treated artifacts was -3.42%. All Group 3 MTMS-treated artifacts had shiny surfaces after treatment. This is a result of not allowing free-flowing polymers to drain sufficiently from the artifacts. As noted with Group 1 and Group 2 wood samples, the resin-forming potential of fresh MTMS is sufficient to preserve the physical appearance and cellular structure of waterlogged wooden artifacts.

In contrast, the resin-forming potential of Q9-1315 is diminished because of the addition of methyl alcohol (50%), isopropyl alcohol (4%) and ethyl alcohol (1%) (0.49% average length shrinkage). Post-treatment diameter shrinkage in these artifacts averaged 9.37%, indicating a substantial increase in shrinkage over MTMS-treated artifacts. The surfaces of the Q9-1315-treated artifacts had a matte, dry appearance after treatment, due to the fact that the less viscous polymer was able to drain more quickly than the MTMS solution

The wood that was treated using the higher percentage MTMS solution looks natural in color and texture following treatment. No surface checking was noted in either the Group 1 wood samples or the archaeological wood. Unfortunately, during the waterlogging process, the natural color of the wood was altered, resulting in a slight grayish cast to the preserved samples. The wood however, is dimensionally stable after treatment in the silane. This experiment indicates that the resins created as the result of condensation can preserve even badly waterlogged wood very well. While C.V. Horie and others have stated that conservation strategies using silicone oils are not reversible, over time the solubility of many adhesives and consolidants currently in common use in conservation are so affected, rendering these techniques also non-reversible.

Additional experiments are needed to determine whether the addition of small percentages of silicone oils might increase the bulking ability of MTMS and Q9-1315, effectively reducing shrinkage. A small percentage addition of a low viscosity silicone oil to Q9-1315 might increase its bulking ability despite its high alcohol content, making it as effective a treatment as MTMS.

BIBLIOGRAPHY

Pearson, C. 1981. ICOM Committee For Conservation Working Group On the Conservation of Waterlogged Wood. In *Proceedings of the ICOM Waterlogged Wood Working Group Conference*, Ottawa, Canada, 1981. 7-9.

McCawley, J. C., D. W. Grattan and C. Cook. 1981. Some Experiments on Freeze-Drying: Design and Testing of a Non-Vacuum freeze Dryer. In *Proceedings of the ICOM Waterlogged Wood Working Group Conference,* Ottawa, Canada, 1981. 253-262.

Grattan, D. W. And C. Cook. 1984. A Practical Comparative Study of Treatments for Waterlogged Wood: Part III: Pretreatment Solutions for Freeze-Drying, Waterlogged Wood, Studies in Conservation. In *Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference*, Grenoble France, 1984. 219-239.

Hoffmann, P. 1984. On the Stabilization of Waterlogged Oakwood with PEG Molecular Size Versus Degree of Degradation. In *Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference,* Grenoble France, 1984. 95-115.

Ginier-Gillet, A., M. Parchas, R. Ramiere and Q. K. Tran. 1984. *Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference*, Grenoble France, 1984. 125-137.

Bronstein, A. 1981. The Chemistry of Polyethylene Glycol. In *Proceedings of the ICOM Waterlogged Wood Working Group Conference*, Ottawa, Canada, 1981. 279 - 285.

Mills, J. S. and R. White. 1994. *The Organic Chemistry of Museum Objects*. Butterworth-Heinemann Publishers, Linacre House, Jordan Hill, Oxford, England.

Horie, C. V. 1999. *Materials for Conservation, Organic Consolidants, Adhesives and Coatings*. Butterworth-Heinemann Publishers, Linacre House, Jordan Hill, Oxford, England.

Wilson, M. A., I. M. Godfrey, J. V. Hanna, R. A. Quezada, and K. S. Finnie. 1993. *The Degradation of Wood in Old Indian Ocean Shipwrecks*. Geochem 20 (5): 599-610.

Hamilton, D. L. 1996. *Basic Methods of Conserving Underwater Archaeological Material Culture*. U.S. Department of Defense Legacy Resource Management Program, United States Department of the Navy, Washington, D.C. 26.

ACKNOWLEDGMENTS

Funding from the National Center for Preservation Technology and Training made this research possible. The author would also like to thank Dow Corning Corporation for their on-going support of research at the Archaeological Preservation Research Laboratory. I would like to thank Dr. Robert Taylor, Research Instrumentation Specialist for Nuclear Magnetic Resonance, Department of Chemistry at Texas A&M University, for his assistance in interpreting spectral data.

ABOUT THE AUTHOR

Wayne Smith is an Assistant Professor in the Nautical Archaeology Program in the Anthropology Department at Texas A&M University and director of the Archaeological Preservation Research Laboratory (APRL). He received his BA in anthropology at the University of Western Ontario, in London, Ontario, Canada. He also studied plant biology and conducted wood conservation experiments under Dr. Grayson, Biology Department, University of Western Ontario. He received his Ph.D. in anthropology from Texas A&M University, College Station, Texas. He worked as an archaeologist and conservator for several seasons at Port Royal, Jamaica, on the excavation of the 17th-century port community, jointly conducted by the Jamaica National Heritage Trust, Texas A&M University and the Institute of Nautical Archaeology. His post-doctoral research was conducted at Dow Corning Corporation in Midland, Michigan, where he developed new technologies for archaeological conservation and industrial applications. To date, he has been awarded three patents for his work with polyethylene glycol and silicone oils.